NON-NEWTONIAN FLOW OF SOLUTIONS OF HIGH MOLECULAR WEIGHT POLYMER IN EXTREMELY VISCOUS SOLVENTS

RAGNER STROMBERG

UNIVERSITY OF UPPSALA
UPPSALA, SWEDEN

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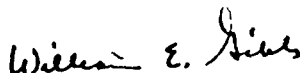*UNIVERSITY OF UPPSALA*
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FOREWORD

This report was prepared by the University of Uppsala, Uppsala, Sweden under Contract AF 61(052)-392. This contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Dr. W. E. Gibbs acting as project engineer.

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This technical report has been reviewed and is approved.

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Recent theoretical work has predicted that the intrinsic viscosity of very long chain polymers in viscous solvents should increase with increasing shear gradient. Highly viscous solvents are required to develop sufficient shearing forces to overcome the inner viscosity (rigidity) of the polymer coil.

This report concerns experimental work directed toward examination of the theory. Two polyphenylene oxide fractions, 1.29×10^6 and 3.45×10^5 molecular weight, in pyralene and two polyisobutylene fractions, 6.0×10^6 and 1.85×10^6 molecular weight, in paraffin oil, were measured in precision equipment which covered five velocity gradient ranges. The maximum shear stresses for pure water, paraffin oil and pyralene are 640, 2600 and 3900 dynes/cm^2.

In these solvents no increase in intrinsic viscosity, as predicted, was observed. Although more information is required before the theory can be fully evaluated, it is suggested that the proposed treatment of gradient dependence does not take into account sufficiently the inner viscosity of the macromolecular coil and anisotropic hydrodynamic interaction.

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INTRODUCTION

The dependence of viscosity on shear gradient has been studied extensively for a wide variation of polymer solutions. Several theoretical treatments have also been published in this field. (References 1, 2, and 3) A recent theory by Peterlin (Reference 4) predicts an interesting new behaviour for solutions of very long chain molecules in extremely viscous solvents. This amounts to an increase of the intrinsic viscosity over a limited range with increasing shear gradient instead of the ordinary steadily decreasing tendency. This result is derived from a detailed consideration of the hydrodynamic interaction between chain elements at various coil extensions. The reason for using highly viscous solvents is to assure large shearing forces to overcome the inner viscosity (rigidity) of the macromolecular coil.

The first attempt to check this theory experimentally was made by Wolff (Reference 5), who used polystyrene ($M \approx 10^7$) dissolved in a mixture of chlorinated diphenyls of viscosity $\eta_0 \approx 1$ P. No increase of the intrinsic viscosity could, however, be detected. Results from measurements in low and moderately viscous solvents also show this general behaviour. (References 6, and 7) Selby and Hunstad (Reference 8), in investigating mineral oils ($\eta_0 \approx 350$ P) that had been "improved" with a macromolecular component, obtained an increase of viscosity with increasing shear gradient. Further experimental evidence for this behaviour was obtained by Peterlin et al. (References 9, and 10) with various polymers dissolved in solvents with viscosities of about 10 P.

As the experimental results published thus far show large deviations from each other further measurements have been carried out on highly viscous systems in the present work.

EXPERIMENTAL

1. POLYETHYLENEOXIDE IN PYRALENE 1498.

Two samples of polyethyleneoxide (PEO) have been used, one of which was kindly provided by the Union Carbide Chemicals Company. The polymer was fractionated by dissolving it twice in carbontetrachloride and precipitating with petroleum ether. The precipitates were then dissolved in water and these solutions were freed from remaining gel particles by centrifugation in a preparative Spinco Ultracentrifuge for one hour at 20,000 and 30,000 r.p.m. respectively and finally freeze-dried. The molecular weights were determined by means of the Staudinger equation for water solutions at 30°C (Reference 11):

$$[\eta] = 1.25.10^{-4}.M^{0.78}$$

Measurements gave $[\eta] =$ 7.30 and 2.60 dl/g, which corresponds to the molecular weights 1,290,000 (PEO I) and 345,000 (PEO II). The degrees of polymerization, which are also very important as they enter into the theory, are 29,000 and 7,800.

The solvent, Pyralene 1498, is the same one that was used by Peterlin et al. Its viscosity is extremely temperature dependent being 2.2 P at 25°C, 5.4 P at 20°C and 12.0 P at 15°C. Since it is desirable to attain as high a solvent viscosity as possible the measurements have been performed at 15°C. PEO does not dissolve in Pyralene at room temperature. At 60°C and during continuous stirring, however, the dissolving process is reasonably fast. The solutions are stable down to 15°C. The possible degradation of the polymer has been checked by repeated measurement on a solution stirred for an additional equally long time and was found to be negligible.

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2. POLYISOBUTYLENE IN PARAFFIN OIL.

The polyisobutylene (PIB) samples have been purified and fractionated by dissolving in cyclohexane, centrifuging at 20,000 r.p.m. for one hour, precipitating the polymer with acetone and finally drying the precipitate. The molecular weights were determined by light scattering in n-heptane solution and found to be $6.0.10^6$ (PIB I) and $1.85.10^6$ (PIB II) corresponding to D.P.'s of 106,000 and 33,000 respectively. Polyisobutylene is not easily soluble in paraffin oil but can be brought into solution by a special technique. The polymer is first dissolved in cyclohexane after which paraffin oil is added. The cyclohexane is then pumped off under continuous gentle stirring at about 50°C.

The viscosity of paraffin oil is 2.5 P at 15°C.

3. MEASUREMENTS IN LOW VISCOSITY SOLVENTS.

In order to get a complete picture of the gradient dependence measurements, they were carried out in low viscosity solvents. Thus solutions of PEO I in water and PIB I in cyclohexane were examined at 25°C, where the solvent viscosities are both equal to 0.89 cP.

4. INSTRUMENTAL.

All measurements in high viscosity solvents were performed at 15°C and those in low viscosity solvents at 25°C. Stock solutions were made up by weight and diluted to the required concentrations by weighing. At least five different concentrations were measured for each fraction.

Different types of viscometers were used to cover different velocity gradient ranges. In the high region special high-pressure Ostwald viscometers were used, which allowed a variation in driving pressure between 10 and 100 cm Hg in eight steps by means of a mercury manostat (Reference 12). The capillary radii were chosen so that suitable flow times were provided for solvents with quite different viscosities. An extrapolation to zero gradient has been performed from data of an ordinary Ubbelohde viscometer with four bulbs. Apparatus constants for the various viscometers are given in Table 1. On account of the high viscosity of the solvents only relatively low values of shear rates can be attained. If, however, instead of the shear rates the shear stresses are given the situation is altered. The maximum shear stresses for pure solvent are 640, 2600 and 3900 dynes/cm^2 for water, paraffin oil, and Pyralene 1498.

Appropriate kinetic energy corrections were applied to the η_r-values when necessary. Furthermore the viscosity and velocity gradient values were corrected to the true values at the capillary wall by the method introduced by Weissenberg. (Reference 13)

RESULTS

The general tendency of the curves obtained in this investigation is shown in Figure 1, where the relative viscosity is given as a function of velocity gradient for different concentrations of PEO II in Pyralene 1498. The same steady decrease in viscosity with increasing gradient is also found in the experimental curves for the other fractions. From η_r versus q curves η_r-values were read at fixed gradients in the regions measured. Figure 2 shows a η_{sp}/c vs c plot for the data in Figure 1. The results at low gradients from the Ubbelohde viscometer are also given in Figure 2. Extrapolations to zero concentration are easily performed giving the intrinsic viscosities, $[\eta]$, with good precision. The intrinsic viscosity can accordingly be determined as a function of velocity gradient q. In Figure 3 the relative intrinsic viscosity $[\eta]_r = \dfrac{[\eta]_q}{[\eta]_o}$, where $[\eta]_q$ and $[\eta]_o$ are the intrinsic viscosities at gradients q and 0 respectively, is plotted vs. q for a number of different systems. The figure reveals fundamental divergences between the systems. The high molecular weight fraction of PIB in the highly viscous solvent does not seem to reach any saturation value within the gradient range covered. The minimum at the beginning of the curve is to be noted. It will be discussed later. The other systems, however, show considerable initial reductions of $[\eta]_r$, whereas the slopes of the curves are rather small at higher values of q. The experimental results for all systems investigated are summarized in Table 2.

DISCUSSION

The various theories in this field deal with the relative intrinsic viscosity $[\eta]_r$ as a function of the parameter $\beta_o = \dfrac{M[\eta]_o \, \eta_o q}{RT}$, where M = molecular weight, η_o = viscosity of the solvent, R = gas constant and T = absolute temperature. The models applied are generally rather restricted. Thus, the theory by Peterlin (References 4, 14, and 15) considers the effect of non-uniform expansion of the macromolecular coil but presupposes gaussian character of interchain distances, isotropic hydrodynamic interaction and complete flexibility of the coil. By means of a detailed calculation of the influence of non-uniform expansion of the coil on the hydrodynamic interaction between chain elements Peterlin predicted, in special cases, an increase of $[\eta]_r$ with increasing β_o i.e. increasing velocity gradient. This is true only when the solvent viscosity is extremely high ensuring large hydrodynamic forces during streaming and the molecule is very long making considerable coil extension possible.

These conditions are met with in the present investigation as can be seen from the figures given in the experimental part.

In Figure 4 experimental results on four systems are compared with Peterlin's theoretical curves (P_x), which correspond to various numbers (x) of Kuhn-elements in the chain. Curves are only given for the higher molecular weight fractions as these are expected to account for the greatest effects. Considering the degree of polymerization of PEO I (29,000) it is most probable that the number of Kuhn-elements in the chain is between 1,000 and 10,000 equivalent to 29 and 2.9 monomer units in each element. A theoretical curve in this range would exhibit an obvious minimum. No minimum is observed for this system and furthermore the curve is located between P_{100} and P_{1000}. The inconsistency with the theory is accordingly very pronounced in this case in spite of a solvent viscosity of 12 P. Water solutions of PEO I of course show the usual behaviour with decreasing viscosity over the whole range.

The system PIB in paraffin oil exhibits a surprisingly small gradient dependence in the range $\beta_o < 50$. A slight minimum in the curve can be observed at about the appropriate β_o -value but the initial drop in $[\eta]_r$ is not as marked as in the other cases. With a D.P. of 106,000, however, a manifested rise would occur as β_o exceeds 10. The measurements have been extended to $\beta_o \approx 300$ without any perceivable increase of $[\eta]_r$. PIB II in paraffin oil shows approximately the same gradient dependence as PEO I in water, the curve not having any minimum. Evidently the PIB-system also displays considerable discrepancy from theory.

Looking at the relative positions of the curves in Figure 4, a puzzling effect appears. PIB I in paraffin oil solution must be more flexible (has a smaller gradient dependence) than in cyclohexane solution, which is in accord with theoretical predictions. Regarding PEO I in Pyralene and water solutions the conditions are reversed in that the curve corresponding to the highly viscous solvent shows a steeper descent. No explanation for this behaviour can be found.

The most obvious explanation for the reported discrepancies is the omission of an inner viscosity term in the theoretical treatment. Since the inner viscosity, is a measure of the rigidity of the macromolecular coil, it has a large influence on the gradient dependence of viscosity. If the coil is not completely flexible, the rigidity would cause a steeper descent of $[\eta]_r$ and prevent the upturn at higher β_o. This explanation seems plausible in the case of PEO. According to Kuhn and Kuhn (Reference 1) a completely free draining and flexible coil would not show a gradient dependence. This fact can be related to the PIB-curve as PIB is a flexible molecule, and gives an explanation to the small gradient dependence.

As was mentioned in the introduction Peterlin et al. (References 9, and 10) have obtained experimental results in accordance with the proposed theory for a number of different systems. A pronounced rise in apparent viscosity with increasing driving pressure was detected, for instance, for Pyralene solutions of polymethylmethacrylate (PMMA) (Reference 9). The curves can be seen in Figure 5 together with the present data on PEO I in the same solvent. The different behaviour of the two systems is most striking. Comparison between the D.P. of the polymers reveals the D.P. of PEO I to be 70 percent that of PMMA, which is not enough to account for the great divergence of the two sets of curves. There is probably a profound difference in hydrodynamic behaviour between the polymers. More experimental data on different systems must be available before any further conclusions can be drawn from the present measurements.

CONCLUSIONS

The present results indicate that the gradient dependence of viscosity probably cannot in all instances be treated by considering only one isolated effect, in this case non-uniform expansion. It is necessary to take into account additional significant factors such as the inner viscosity of the macromolecular coil (References 1, and 2) and anisotropic hydrodynamic interaction (Reference 3). A complete quantitative treatment must involve the simultaneous consideration of all contributing factors. This very complicated problem has not yet been solved.

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TABLE 1.

APPARATUS CONSTANTS FOR THE DIFFERENT VISCOMETERS

Viscometer	Solvent	Range of maximum shear rates (sec^{-1})	Capillary length (cm)	Capillary radius (cm)
B 1	water	370-1500	30.0	0.028
	cyclohexane	280-1150		
M 16	Pyralene	1.5-5.8	30.0	0.117
	paraffin oil	4.3-16.9		
H 1	water	8000-71000	9.7	0.010
	cyclohexane	8000-71000		
H 4	Pyralene	36-325	9.7	0.062
H 5	paraffin oil	115-1045	10.1	0.042

TABLE 2
INTRINSIC VISCOSITIES AT DIFFERENT
VELOCITY GRADIENTS FOR VARIOUS SYSTEMS

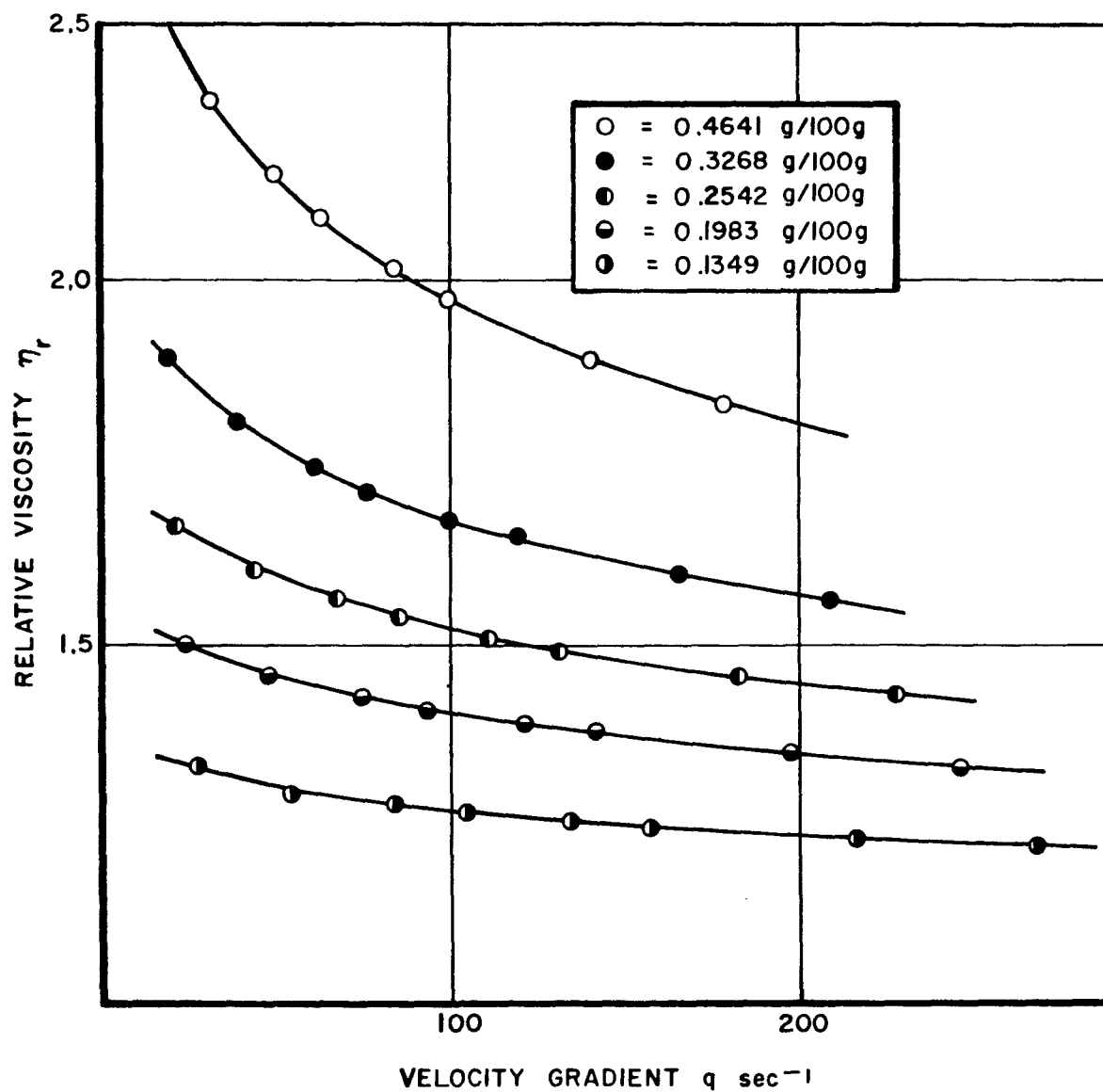| System	q $(\sec^{-1})$	$[\eta]$ (ml/g)	System	q $(\sec^{-1})$	$[\eta]$ (ml/g)
PEO I in Pyralene	0	474	PEO II in Pyralene	0	189
	2	397		2	180
	25	281		25	156
	75	271		75	141
	200	244		200	118
PEO I in water	0	747	PIB I in paraffin oil	0	720
	1000	693		6	671
	5000	660		10	635
	10000	615		40	658
	25000	561		100	644
	50000	556		200	608
				400	549
				700	498
PIB II in paraffin oil	0	356	PIB I in cyclohexane	0	1460
	6	350		600	1250
	100	279		5000	987
	200	264		10000	975
	400	259		25000	956
	700	257		50000	904

Figure 1. The Gradient Dependence of Relative Viscosity for Different
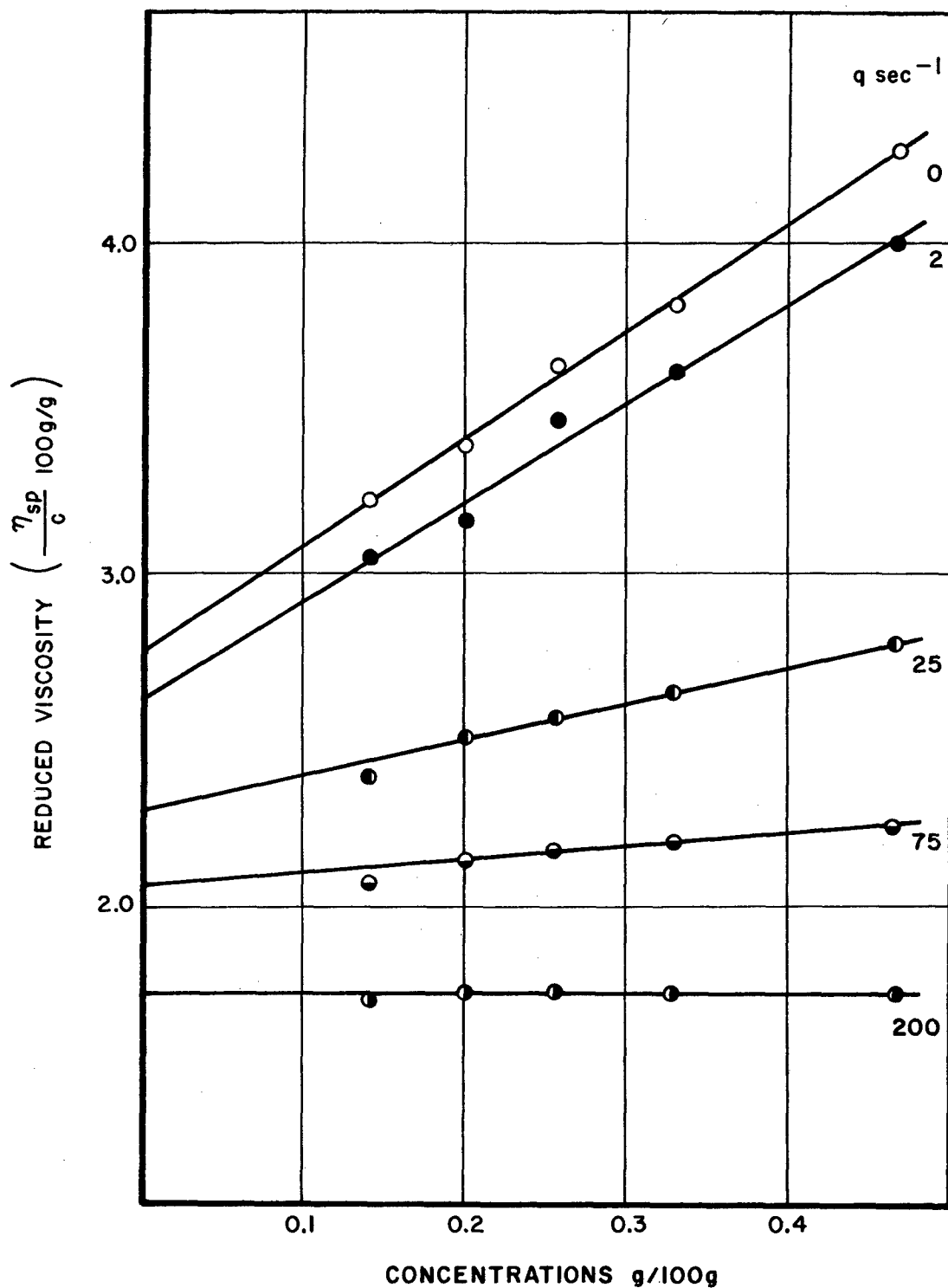Concentrations of PEO II Dissolved in Pyralene

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Figure 2. Reduced Viscosity (η_{sp}/c) as a Function of concentration (c) with the Velocity Gradient as a parameter for PEO in Pyralene.
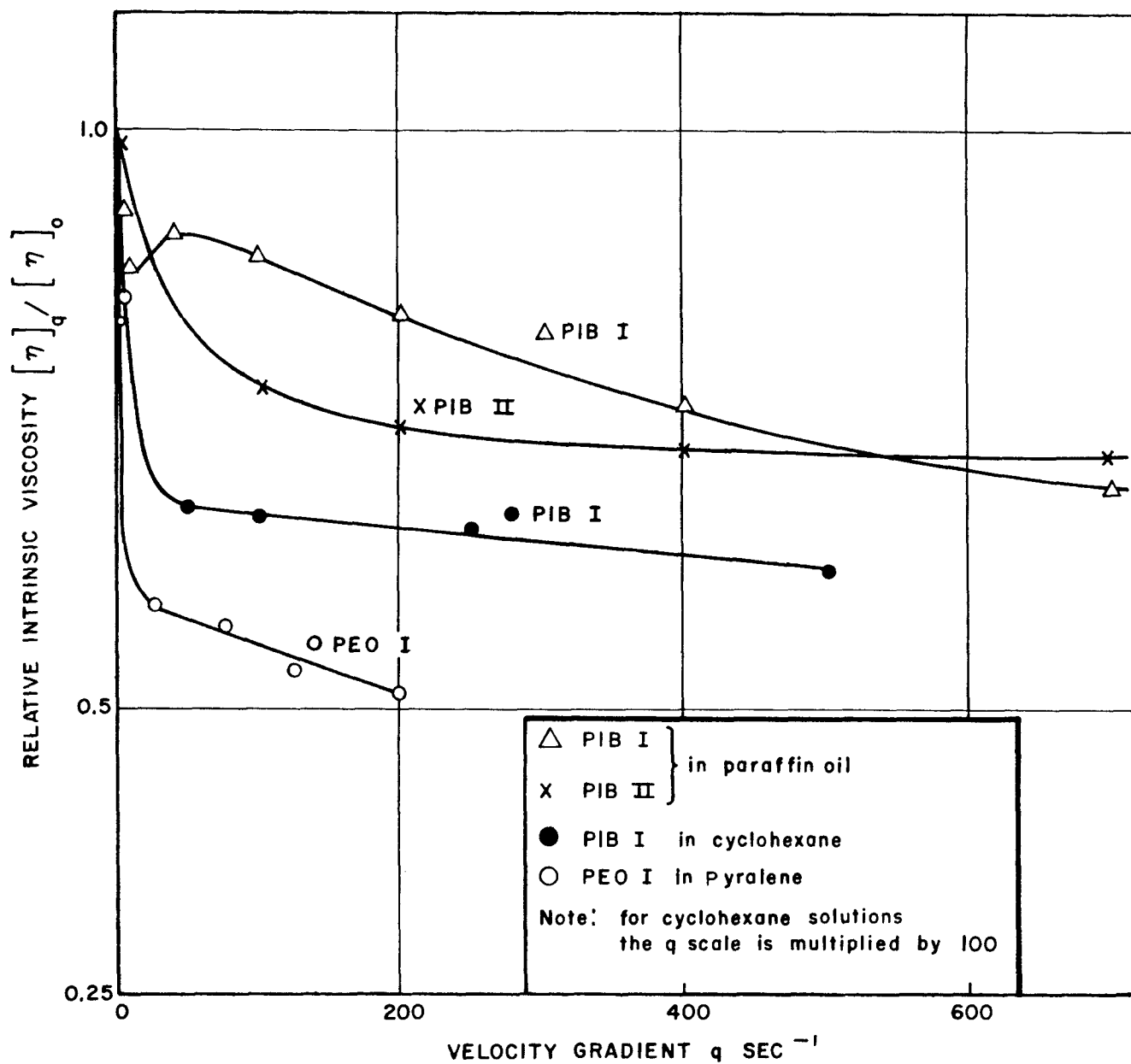
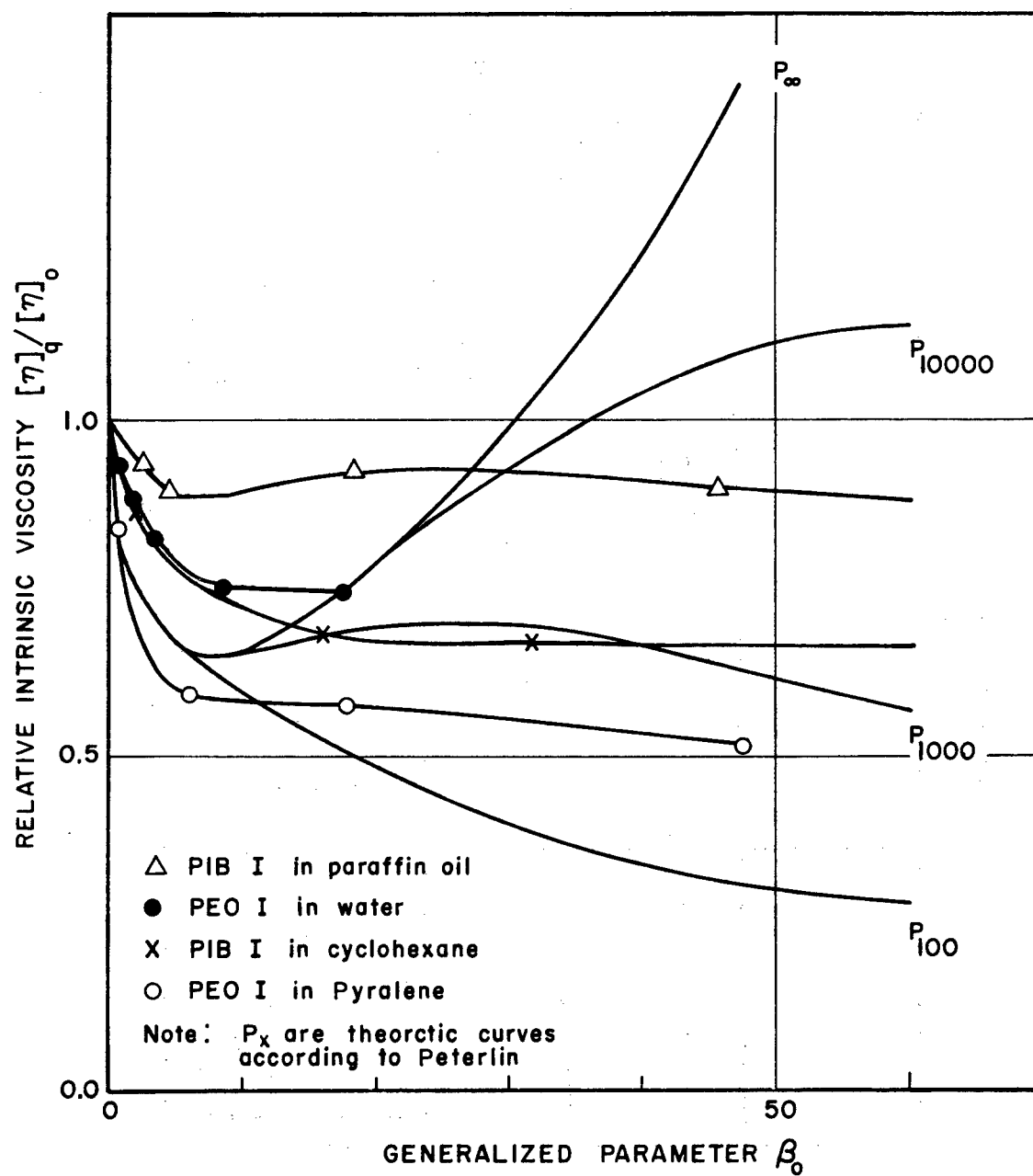Figure 3.   Relative Intrinsic Viscosity vs. Velocity Gradient

Figure 4. Relative Intrinsic Viscosity Vs. Generalized Paramater β_0.
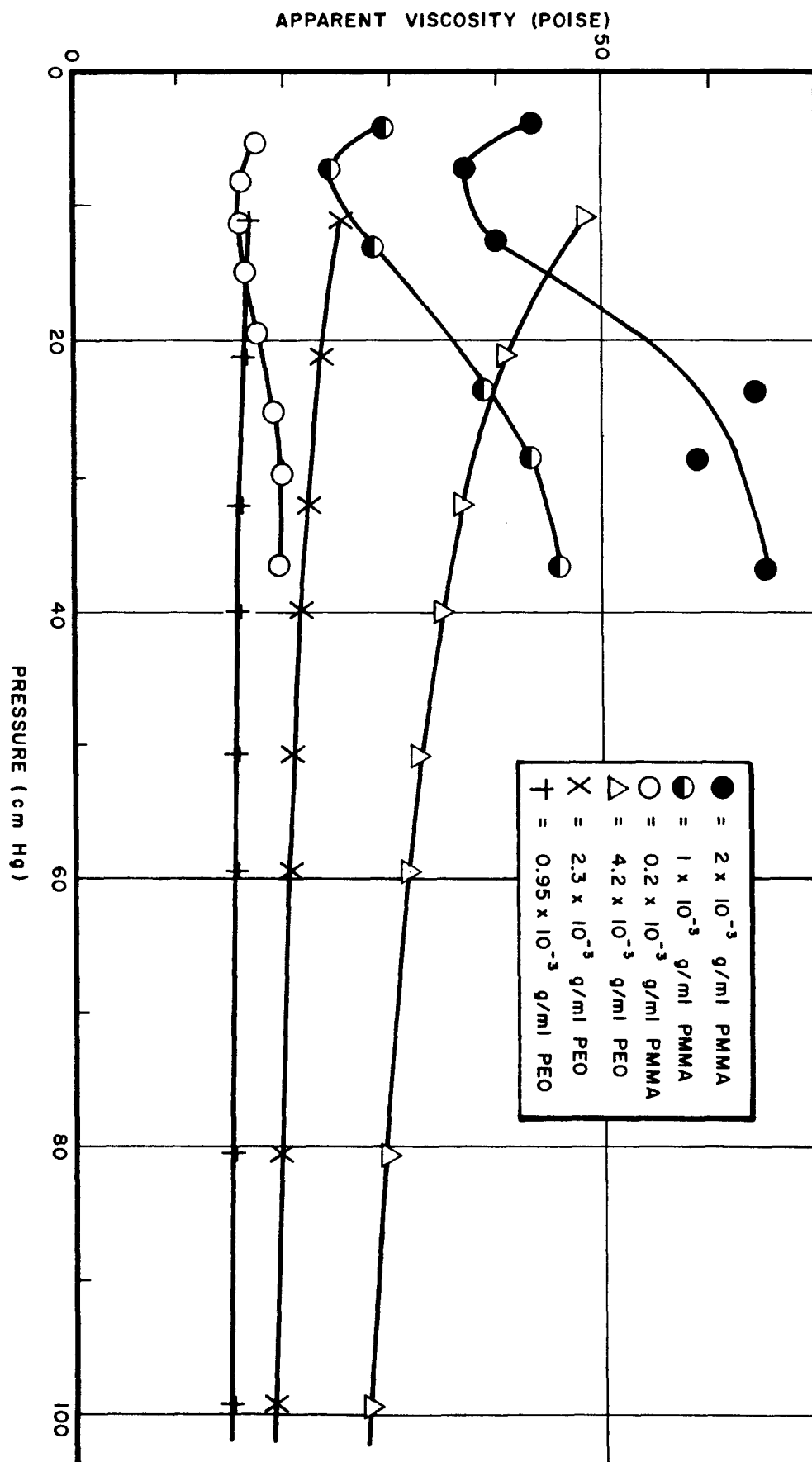
Figure 5. Apparent Viscosity Vs. Driving Pressure at Different Concentrations of PMMA and PEO in Pyralene Solution

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13. ABSTRACT

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This report concerns experimental work directed toward examination of the theory. Two polyphenylene oxide fractions, 1.29×10^6 and 3.45×10^5 molecular weight, in pyralene and two polyisobutylene fractions, 6.0×10^6 and 1.85×10^6 molecular weight, in paraffin oil, were measured in precision equipment which covered five velocity gradient ranges. The maximum shear stresses for pure water, paraffin oil and pyralene are 640, 2600 and 3900 dynes/cm^2.

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